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Synthetic Grease

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I. HISTORICAL PERSPECTIVES

Lubricants greatly reduce the frictional burden that nature levies against people and machines when two objects in contact are moved relative to each other. The recognition by ancient engineers that certain natural products were effective in facilitating the movement of massive objects and also reduced the demand for muscle power was indeed the genesis of today's lubricant industry.

The archaeological record indicates that stone-building civilizations routinely used olive oil beneath wooden planks to reduce the friction and work needed to transport massive stones. Moreover, in the ancient transportation sector, animal fats were used in conjunction with inorganic fillers to reduce the frictional forces between the bearing surface and shaft on chariot wheels. These discoveries clearly indicated that lubricants were a viable engineering tool to many early societies; however, the original use of any lubricating substance probably has its roots in some forgotten cave. It may have been a prehistoric cave dweller who first realized that the slippery residue left on his hands after dinner would increase the effectiveness of his spear when applied to the point. Perhaps the first use of a lubricant was to bring down a woolly mammoth.

Thoughtful people throughout the ages have always sought methods to reduce the effort required to accomplish a task. It is not uncommon even today to see a retired carpenter instructing an apprentice on the merits of applying wax to the tips of finish nails to successfully drive the fastener into an obdurate stair tread made of oak.

There is one other aspect pertaining to the discovery of lubricant in the hubs of ancient wheeled vehicles that is both technically interesting and fascinating. Along with animal fats (fats are mixed esters of glycerol), calcium oxide and lime were also identified by chemical methods as the grease used in chariot wheel hubs. Although the combination of ingredients may appear quite inconsequential a priori, closer scrutiny reveals some real magic. The ramifications of the serendipitous mixture can be explained as follows.

Animal fat is added to the axle and wheel hub along with calcium oxide. During operation, frictional heating generates the thermal energy necessary to activate a chemical reaction between the lime and fat, producing a quasi in situ saponification. The resultant product has lubricating

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characteristics superior to those of the original ingredients separately and also has a higher dropping point than the fat—and all this was accomplished millennia before the great French chemist Lavoisier elucidated the chemistry involved in displacement reactions. For a chemist specializing in lubricants, the realization that a substance with modern greaselike attributes was discovered in chariot wheel hubs is tantamount to a computer scientist finding a 1950s vintage computer chip among the Dead Sea scrolls.

II. THE NATURE OF SOLIDS AND THE UTILITY OF GREASE

Much of the material world that humans find suitable for fabricating useful products is solid. Spacecraft, automobiles, and bicycles are all made from solids. However, when two contacting solids are moved tangentially in relation to each other, frictional forces are encountered that act to oppose the motion—friction is nature's way of taxing us for moving something! Although friction is a fundamental property of all matter, it is particularly detrimental in the case of contacting solids, since it usually leads to the unwanted removal of material from one or both of the contacting members. Solids, unlike liquids and gases, are held together by extremely strong forces, and as such these substances have a propensity to bond or adhere strongly when their cleaned surfaces come into contact. On a microscopic scale, all surfaces appear rough.

Profilographic analysis reveals successive maxima and minima, with the peaks often referred to as asperities. Although it may be tempting to assume that the frictional force arises as a result of the interlocking of opposing asperities, this is clearly not the case [8]. According to the advocates of the adhesion theory, the nature of the friction force is in the product of the real area of contact between the contacting surfaces and the shear strength of the softer contacting member. The coefficient of friction, μ, can be expressed as the ratio of a material's resistance to plastic deformation due to shear and that due to compression. This parameter, once determined empirically for a given set of sliding material surfaces [13], can be employed in a variety of engineering and mechanics calculations [14]. Mathematically, the coefficient of friction can be represented as follows:

$$\mu = \frac{S}{P} \tag{1}$$

where S is the strength or the ability of the softer of two contacting materials to resist plastic flow due to shear and P is the compressive strength of the softer material or its ability to resist plastic flow due to compressive loads. Other tribological contributors to the overall frictional force are asperity deformation and the formation of wear debris that plows into the contacting surface. The plowing component often leads to erratic frictional behavior for mated contacts due to its transient nature. The total coefficient of kinetic friction μ, under dry sliding is the sum of the three factors expressed mathematically as follows:

$$\mu_t = \mu_d + \mu_a + \mu_p \tag{2}$$

According to Suh, the relative contribution to the overall coefficient of friction from each of the factors is summarized as in Table 23.1 [15]. It should be noted that if a lubricant is present, the frictional force can be increased dramatically by a fourth factor, viscous drag, created by the lubricant itself.

Greases, on the other hand, are semisolids. Since greases are held together by forces orders of magnitude weaker than the forces that bind solids, they are useful materials to place between solids. In the absence of lubricating greases, rigid materials tend to self-destruct. When solids are rubbed together, heat is generated, causing surface and subsurface electrons to vibrate with

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Table 1 Factors That Affect the Coefficient of Friction

Factor	Symbol	Relative numerical contribution
Asperity deformation	μ_d	0.43–0.75
Asperity adhesion	μ_a	0–0.4
Plowing by wear debris	μ_p	0–1.0

greater amplitude, and at some critical temperature metallic bonds are ruptured and a wear particle is created. Greases are useful as lubricants because they reduce friction and wear, dampen vibration and noise, seal out contaminants (including water), remain where applied under rigorous temperature excursion, and serve as oil reservoirs, releasing oil as conditions warrant. Moreover, under conditions of low shear they exhibit a high apparent viscosity, but approach the viscosity of the base fluid component at sufficiently high rates of shear.

III. THE COMPOSITION OF SYNTHETIC GREASE

All lubricating greases, including synthetics, consist of two fundamental components: a base fluid representing the principal ingredient in the formulation and a thickening agent that is used to immobilize the fluid. The concentration of thickener determines the consistency of the finished product; however, it is the nature of the oil that determines whether the grease will be classified as a synthetic. Although all greases contain an oil portion and a thickener, the possible oil and thickener combinations and the specific additives (e.g., antioxidants, antiwear, anticorrosion, or extreme pressure agents) employed provide manufacturers with a great deal of flexibility in formulating products with many different physical and chemical attributes. The lubricating oils commonly used to formulate synthetic lubricating greases are listed in Table 23.2, along with some of the notable characteristics of each fluid.

Although it is the oil that characterizes a grease as synthetic, the thickener type determines the identity of the grease. For example, a lubricating grease prepared from a poly(α-olefin) oil [poly(α-olefins) are commonly referred to as synthetic hydrocarbons, abbreviated as SHCs or PAOs] thickened with lithium 12-hydroxystearate would be referred to as lithium-soap-thickened synthetic hydrocarbon. An ester thickened with an organomodified clay would be described as a clay-based synthetic ester.

Synthetic greases are prepared from both organic and inorganic thickeners (see Table 23.3). Organic thickeners are prepared from the reaction of a suitable alkali metal with either high molecular weight carboxylic acids or fats. A chemical reaction that takes place in the oil used in formulating the grease is referred to as in situ neutralization or in situ saponification, depending on whether an acid or fat is the coreactant. Table 23.4 identifies some of the alkali metals commonly used to make greases. The alkali metals are usually reacted with stearic acid, myristic acid, 12-hydroxystearic acid, or hydrogenated castor oil, a triglyceride that liberates 12-hydroxystearic acid during saponification.

Inorganic thickeners, such as chemically modified clay, amorphous silica, and polytetrafluoroethylene, can also be used to form grease, but without the need for a chemical reaction for grease formation to occur. The efficacy of a particular thickener to convert a synthetic oil into grease depends on the ultimate surface area of the thickener, its ability to bond with hydrogen, and its tendency to associate with the fluid on a molecular level. The thickener must have an affinity for the base fluid that is intermediate between the forces that lead to greater solubility

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Table 2 Lubricating Oils Commonly Used in Synthetic Greases

Fluids	Chapter no., this volume	Characteristics
Diesters	3	Suitable for making grease serviceable to −73°C (−99°F)
Polyol esters	5	Higher viscosity than the diesters with better oxidative stability and less volatility.
Pentaerythritol esters	5	Primarily used to formulate synthetic greases requiring excellent lubricating properties from −40°C (−40°F) to over 177°C (351°F).
Polyglycols	6	These oils, which tend to produce less carbonaceous residue upon degradation, find use in formulating greases for arcing electrical equipment.
Poly(α-olefins) (PAOs)	1	A relatively new class of synthetic hydrocarbon fluid available in a range of viscosities, these oils exhibit improved compatibility with ester-vulnerable thermoplastics and elastomers.
Polybutenes	16	A subset of the synthetic hydrocarbons with better viscosity–temperature characteristics than the PAOs and good properties as tackifier or damping fluid, but with a tendency to degrade under high shear.
Silicones	11	Outstanding thermo-oxidative stability, chemically inert, low and high temperature usefulness, and unmatched viscometric properties as a function of temperature. The viscosity index of one phenylsilicone is over 600.
Halocarbons	10	Chemically inert toward oxygen and possessing excellent innate boundary and extreme pressure lubricating properties, as well as extremely low temperature performance for the lighter viscosity grades.
Polyphenyl ethers (PPEs)	9	Two grades of these fluids are available, a five-ring and a six-ring molecule. The fluids possess exceptional radiation resistance, have outstanding thermo-oxidative stability and high surface energy, and have been used extensively for lubricating noble metal electrical contacts.
Phosphate esters	4	Can be used to manufacture relatively inexpensive greases that are able to resist ignition.
Perfluropolyethers (PFPEs)	8	Synthetic greases formulated from "branched" and "linear" versions of these fluids are inert toward oxygen and all but the most aggressive chemicals. Greases made from these oils have unsurpassed thermo-oxidative stability. The PFPEs with a straight polymer chain morphology ("linear PFPEs") also have excellent viscosity index and low temperature performance.
Multiply alkylated cyclopentanes (MACs)	15	The newest commercially available synthetic fluid, demonstrating exceptionally low volatility under hard vacuum and elevated temperature.

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Table 3 Thickeners Commonly Used in Synthetic Greases

Gellants	Characteristics
Paraffin wax	Low cost; low melting point
Alkali soap	Temperature to 200°C, pumpability, most common thickener
Organoclay	Temperature to 250°C, high loads, incompatible with some polar additives
Alkali complex soap	Temperature to 250°C, pumpability, water resistance
Polyurea	Temperature to 250°C, pumpability, stability, excellent in high load bearings
PTFE	Temperature to 300°C, low coefficient of friction, inert, moderate load only
Silica	Nonmelting, water resistance, low oil separation/good oil retention
Metal oxide	Nonmelting, thermal conductivity, inert

Table 4 Alkali Metals Used to Prepare Alkali Soap Thickened Greases

Alkali	Formula
Lithium hydroxide monohydrate	$LiOH \cdot H_2O$
Calcium hydroxide	$Ca(OH)_2$
Sodium hydroxide	$NaOH$
Aluminum hydroxide	$Al(OH)_3$

and the forces rending to induce phase separation. This mesosolubility is a prerequisite for all successful grease formation.

IV. GREASE MANUFACTURE

Organic greases are usually manufactured in kettles. The vessels range in size from laboratory units capable of manufacturing only 2–5 kg (5–10 lb) per batch to very large units capable of manufacturing 18,000 kg (40,000 lb) of grease in a single operation. Since heat is required to initiate the reaction of the ingredients used to manufacture soap-based grease, or in general to promote the solvency of lubricating fluids and additives, grease kettles are heated. Most are jacketed to accommodate either steam or hot oil. Steam is an advantageous thermal medium because cold water can be circulated through the same jacket to cool the batch on completion of the chemical reaction. The primary disadvantage of heating the grease charge with steam is that high pressure is required to attain temperatures above 230°C (446°F). Aside from steam, oil, electricity, and direct heating are also used to heat grease kettles. Generally, a soap-thickened grease is manufactured by adding a small portion of base oil to the kettle along with all the fatty acid. At this stage, only enough heat is applied to melt the charge. Once the fatty acid has melted into the base oil, an aqueous solution of the alkali metal is added to the kettle incrementally. The addition is carried out in four steps to prevent die reaction mass, which is approxi-

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mately at the boiling point of water, from unexpectedly discharging from the kettle, propelled by the copious quantities of steam that form in the kettle.

The kettle contents are continuously stirred, usually with counterrotating stirrers, to facilitate the dehydration of the soap mass as the reaction proceeds. After dehydration, additional base oil is gradually added to the kettle. The addition of oil must proceed slowly, to maximize proper mixing of the intractable soap mass and the oil being added. After the addition of the required quantity of oil, the kettle contents are heated to some predetermined elevated temperature and maintained at that temperature for several hours. After the heating cycle, the grease is rapidly cooled to optimize the dispersion of the thickener. The rate at which the kettle contents are cooled has a pronounced effect on the finished consistency of the grease. Additives are usually added to the grease after the temperature of the batch has fallen below 100°C (212°F). When the kettle contents have reached room temperature, the grease may be either milled or homogenized. As a final step the grease may be filtered to remove contaminants. Quality control testing usually occurs before the grease is discharged from the kettle for packaging.

V. GREASE CHEMISTRY

A. Preparation of a Synthetic Ester Grease

The following batch workup illustrates the preparation of 100 kg (220 lb) of a synthetic ester grease thickened with sodium myristate. The finished product is to contain 12% thickener. The kilograms of thickener required equals the batch size multiplied by the desired thickener concentration, so that the amount of thickener required is given by

$$100 \text{ kg} \times 0.12 = 12 \text{ kg}$$

The balanced chemical reaction is

$$NaOH + H_3C(CH_2)_{12}COOH \rightarrow NaOOC(CH_2)_{12}CH_3 + H_2O$$

Because the molecular weight of the thickener, sodium myristate, is 226 g/mol, and 12 kg of thickener is needed, the number of moles of each reactant is equal to the number of moles of thickener, to match the one-to-one stoichiometry indicated by the balanced chemical reaction. Therefore, the numbers of moles of sodium hydroxide and myristic acid required are determined from the data in Table 5 as follows:

$$\frac{12{,}000 \text{ g}}{226 \text{ g/mol}} = 53.09 \text{ mol} \tag{3}$$

The sodium hydroxide would be dissolved in sufficient deionized water to completely dissolve the base, and the myristic acid would be added to the reaction vessel along with a small portion of nonsaponifiable petroleum oil. (The reaction cannot be conducted in the presence of

Table 5 Data for Determining Moles of Thickener in Reaction [3]

Ingredient	Number of moles	Amount needed		
		g/mol	kg	(lb)
NaOH	53.09	23	1.221	(2.691)
Myristic acid	53.09	204	10.83	(23.88)

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the ester base oil because esters are susceptible to de-esterification in the presence of strong bases.) When the neutralization reaction is completed and the soap mass has been adequately dehydrated, the thickener is then capable of absorbing the synthetic ester base fluid. The oil is added incrementally to effect proper mixing while the temperature of the kettle contents is maintained at approximately 150°C (302°F). When the total charge of oil has been added to the kettle, the temperature is reduced and the desired additives are added to the grease. The batch is further cooled and discharged from the kettle.

A primary advantage of synthetic lubricants over petroleum-based products is their improved serviceability at elevated temperatures. However, the ability of a lubricating grease to resist excessive softening or melting at extreme temperatures is dictated by the nature of the thickening agent. Most organic soap thickeners melt at temperatures below 230°C (446°F). To overcome the apparent thermal deficiency, complex thickeners are used that do not melt. Dropping points for many complex greases are usually above 260°C (500°F).

B. Preparation of an Aluminum Complex Grease [3]

The preparation of 100 kg (220 lb) of an aluminum complex grease containing a synthetic hydrocarbon base oil can be illustrated as follows:

Batch size	100 k
Thickener content	7.5%
Ratio of benzoic acid to stearic acid	0.8
Ratio of both acids to aluminum	1.9
Thickener required = 100 kg × 0.075 =	7.5 kg
Balanced chemical equation:	
$H_2O + Al(OC_3H_7)_3 + C_{17}H_{35}CO_2H + C_6H_5CO_2H \rightarrow (C_{17}H_{35}CO_2)AlOH(C_6H_5CO_2) + 3C_3H_7OH$	

The amount of each ingredient is determined based on the specified composition of the grease in molar ratios (Table 6). Since the aluminum (as the isopropoxide) is supplied as a 12.7% mixture in oil, the 0.474 kg (1.04 lb) of aluminum would be available in 3.73 kg (8.22 lb) of the commercial product.

To manufacture the grease, the reaction of the ingredients would be carried out in a portion of the synthetic hydrocarbon fluid, after which the remaining oil and additives would be added. Kettles suitable for manufacturing complex aluminum greases must be designed to recover the alcohol liberated by the reaction.

Table 6 Data for Determining Amounts of Ingredients to be Used in Aluminum Complex Grease

Ingredient	Moles	Molecular weight	Batch		
			Unit	kg	(lb)
Stearic acid	1.0	278.6	278.6	5.20	(11.5)
Benzoic acid	0.8	122.0	97.6	1.82	(4.01)
Aluminum	0.94	27.0	25.4	0.474	(1.04)
			401.6	7.49	(16.5)

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C. Polyurea Grease [1]

Although many polyurea greases contain petroleum base oils, these greases deserve mention in a text dedicated to synthetics because of their unique thickener chemistry. The alkyl aryl polyurea thickening agent commonly used is a synthetic high molecular weight polymer that provides the following advantages: a dropping point of approximately 250°C (482°F), excellent water resistance, low oil separation, and an uncanny ability toward shear thinning that renders polyurea grease ideally suited for many rolling-element bearing applications.

D. Organomodified, Clay-Thickened Synthetics

The ability of clay to function as an effective thickener for lubricating fluids is dependent on its surface pretreatment. The addition of a suitable organic compound to the surface of individual clay platelets transforms the material from a hydrophile to an oil absorber. Clay is useful as a thickening agent for grease because of its dispersible lamellar-type structure and ability to hydrogen bond. Individual platelets are only angstroms thick and possess tremendous surface area when efficiently dispersed. Moreover, since a chemical reaction is not required to form a synthetic grease from a clay thickener, these greases can be easier to produce and require less energy to manufacture than soap-based greases. To achieve a viable product, however, the grease formulator must optimize the amount of dispersant and water used to open the individual clay bundles and promote hydrogen bonding. Clays are suitable for thickening hydrocarbons, poly-glycols, and some silicones. However, the suitability of the clay thickener in a particular lubricating medium is predicated on the polarity of the oil and the clay's surface treatment. A clay (alkyl aryl ammonium hectorite) thickened polyglycol grease can be prepared by simply adding approximately 7% clay to the polyglycol, stirring the mixture, then adding to the optimized level of distilled water a propylene carbonate,* and finally passing the pregrease through a mill or high pressure homogenizer to effect gellation.

Although clay-based greases are nonmelting and are often recommended for high temperature applications, sustained usefulness at elevated temperature is limited in all greases by the thermo-oxidative stability of the base oil.

E. Polytetrafluoroethylene-Thickened Synthetic Grease

Polytetrafluoroethylene (PTFE) is one of two thickening agents used for synthetic oils that can be classified as a universal gellant. Polytetrafluoroethylene is capable of forming grease from all of the synthetic fluids mentions in Table 1. The ability of PTFE to thicken oil is due to its low surface tension, surface area, and dispersability in-organic fluids. Greases prepared from PTFE and synthetic fluids are serviceable at extremely low temperatures and are capable of continuous service above 200°C (392°F). Grease prepared from telomers of PTFE are probably the most suitable PTFE-thickened lubricants for long-term lubrication of rolling-element bearings. Because an NLGI grade 2 grease can be prepared from 20% PTFE derived from the telomer dispersion and 40% PTFE is required from the less expensive micropowders, the grease with the greater oil reservoir would be expected to function long after the lubricant with the higher concentration of thickener has become intractable by reason of oil loss. The efficacy of grease is dependent on a favorable balance between the amount of oil and thickener. As the oil-to-thickener ratio changes because of oil separation, oil evaporation, and oil oxidation, the grease is gradually transformed into an intractable mass that fails to lubricate.

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* Propylene carbonate is one of several dispersants used to manufacture clay-based synthetic greases. Acetone and ethanol are also used.

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VI. ADVANTAGES OF SYNTHETIC GREASE

The primary advantages of synthetic grease over petroleum-based products are improved thermo-oxidative stability, wide temperature serviceability, and less change in apparent viscosity as a function of temperature. Each advantage can be elaborated. Oxygen is a pernicious molecule capable of rapidly degrading organic lubricants at elevated temperatures, either by abstracting hydrogen from vulnerable sites along the lubricant molecule or by directly reacting with sites of unsaturation. Since oils used to formulate synthetic greases are virtually free of unsaturation and are synthesized to be resistant to oxidative attack, synthetic greases, as a class, greatly outperform their nonsynthetic rivals under severe oxidizing conditions. Moreover, silicones and perfluoropolyethers demonstrate superior resistance to oxidative degradation at temperatures above 150°C (302°F) after years of exposure. Similar exposure would transform petroleum-based products into intractable polymers commonly referred to as sludge or varnish.

With selected oils, synthetic grease can be formulated with unsurpassed ability to remain pliable at –54°C (–65°F) while not deteriorating or excessively evaporating at temperatures above 1778C (3518F).

Adequate viscosity under operating conditions is, in the authors' judgment, the most important property any lubricant can possess. Without it, moving surfaces are destined for self-destruction regardless of how well the grease is fortified with special additives. Greases made from synthetic oils maintain their apparent viscosity as a function of temperature better than nonsynthetics.

Additionally, synthetic greases, as a class, are more compatible with various engineering thermoplastic and elastomers. There is, however, a notable exception, namely the synthetic esters, which adversely affect certain vulnerable plastics such as acrylonitrile butadiene styrene (ABS), polyvinyl chloride (PVC), polystyrene, polysulfone, and polyphenylene oxide (ref 10). Because of the ability of low viscosity oils to permeate into a rubber matrix and thus cause swelling, it is always prudent to make a compatibility determination when the use of a lubricating fluid with elastomers is contemplated.

Special functional properties are achievable with greases made from particular base oils or gellants. For example, certain silicone-based greases can be prepared with specific indices of refraction; electrically conductive gellants can be used to prepare a grease with low electrical resistivity. Special synthetic greases prepared from polyphenyl ethers demonstrate superior resistance to ionizing radiation, and are not degraded at 300°C at oxygen pressures of 3500 Pa.

A frequently overlooked advantage of synthetics is the consistency of their chemical and physical properties from batch to batch, and their relative freedom from various impurities. Synthetic lubricants, unlike many petroleum lubricant products, are virtually odorless and do not contribute to the olfactory assault in the workplace.

VII. COST OF SYNTHETIC GREASES

The principal disadvantage of synthetic greases over petroleum-based greases is cost. Compared to many nonsynthetic products, the prices of synthetics are truly stratospheric; however, demands placed on modem devices have made the higher costs palatable to many firms. As an extreme example, popular sodium complex, high speed spindle bearing grease formulated from a petroleum oil is commercially available at less than a dollar per pound. As with any engineered material, synthetic greases can be considered only when the operating requirements dictate the need tor very specialized lubricants. However, most synthetic greases are typically priced between $5 and $50 per pound in 16 kg (35 lb) containers. Synthetic lubricants formulated from perfluoropolyether can approach $1000 per pound. Low volumes of specialized formulations

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Table 7 Lubricant Cost Versus Volume of Lubricant Used

Amount of grease per device: hemisphere diameter (mm)	Grease mass per 100,000 units[a]		Grease cost per device in U.S. currency at $22/kg ($10/1b)
	kg	1b	
1	0.026	0.058	0.00058 cent
2	0.21	0.46	0.0046 cent
3	0.73	1.6	0.016 cent
5	3.3	7.2	0.072 cent
10	26	58	0.58 cent

[a] For grease density = 1 g/cm^3.

requiring a great deal of testing for aerospace, computer, or medical applications can command even higher prices. In many applications, as illustrated in Table 7, the cost of the grease per unit of equipment is negligible compared to the value added to that equipment in terms of longer equipment life, improved reliability, lower torque, lower acoustic noise, and other functional advantages.

VIII. GREASE TESTING

A. Industry Standard Test Methods

The American Society of Testing and Materials (ASTM), along with its European and Japanese counterparts, has standardized a vast number of tests used to measure specific chemical or physical properties of grease. Some of these tests measure characteristics particular to the composition, while other tests are more suitable for assessing batch-to-batch variability. Volatility per D-972, water washout per D-1264, and the four-ball wear test per D-2266 are examples of tests that measure properties of the grease inherent to the formulation. Some variation in these properties is possible, due to either the product or the test method, but the magnitude of the variation should be minor from one batch to the next. However, it is necessary and prudent to conduct tests that are sensitive to the composition of a synthetic grease at established intervals. The specific interval ought to be determined after consultation with customers.

Because grease manufacturers cannot exercise absolute control over the chemical reactions or processes that produce grease, certain physical tests should be conducted on each batch of grease to monitor important grease characteristics. These tests may be categorized as batch specific and can be used to monitor the homogeneity of the product as a function of time. Such tests are a benefit for statistical process control. Table 8 lists the tests that should be conducted on a production batch basis.

The consistency of a grease measures its resistance to deformation under an applied force. Measures of consistency attempt to quantify plastic behavior, as measures of viscosity try to delineate fluidity. The National Lubrication Grease Institute (NLGI) has developed a numerical scale to classify the consistency of greases based upon their worked 60-stroke penetration values. Semifluid greases have a triple zero rating, while the hardest greases would receive a rating of 6. The nine NLGI ratings or grades are given in Table 9. Properties that can be tested to qualify a new grease formulation without need for batch-to-batch testing are presented in Table 10.

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Table 8 Synthetic Grease Properties That Tend to Vary Batchwise

Property	Method	Purpose
Unworked penetration	ASTM D-217	Measures the consistency of the grease prior to the input of mechanical energy. This is what the customer's pump is required to transfer.
Worked penetration, 60 strokes	ASTM D-217	Measures the mechanical stability of the grease. Excessive change may signal problems in applications imparting high shear to the grease.
Oil separation	Federal Test Method 791B, method 321.2	This test assesses the amount of oil released from the grease structure after 30 h at 100°C (212°F).
Evaporation	ASTM D-972	Measures evaporation of any volatile ingredients in the grease or residual by-products generated during manufacture.
Dropping point	ASTM D-2265	Determines the high temperature attainable before a drop of oil separates from the grease.

B. Analytical and Application-Specific Test Methods

Modern analytical laboratory equipment, with integrated computer software, can provide key insights into the makeup and function of synthetic lubricant formulations. Spectroscopic methods such as Fourier transform infrared (FTIR) spectroscopy often are used to look for molecular signatures for various gellants, base oil species, and additives. Thermogravimetric analyzers (TGA) and pressure differential scanning calorimeters (PDSC) find use in detailed quantitative analysis of melting points, phase changes, and thermo-oxidative stability of lubricant formulations.

Application-specific testing is often performed by lubricant formulators to prescreen product candidates for OEM customers prior to full-scale lubricant qualification tests in the actual OEM

Table 9 Measures of Grease "Stiffness"

NLGI grade	ASTM worked penetration, 60 strokes	Analogous consistency for household food item (unworked penetration) ref. [9]
000	445–475	Ketchup
00	400–430	Applesauce
0	355–385	Brown mustard
1	310–340	Tomato paste
2	265–295	Peanut butter
3	220–250	Vegetable shortening
4	175–205	Frozen yogurt
5	130–160	Smooth paté
6	85–115	Cheddar cheese spread

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Table 10 Synthetic Grease Properties That Are Not Expected to Vary Appreciably by Batch

Property	Method	Purpose
Oxidation stability	ASTM D-942	Measures the thermo-oxidative stability of the lubricant at elevated temperature under pure oxygen pressure. The reduction in pressure indicates oxidation.
Wear preventive characteristics	ASTM D-2266	In this test to determine the boundary lubricating properties of the lubricant, a loaded, rotating steel ball is forced against three stationary balls at an elevated temperature for one hour. The resulting average wear scar is used to assess the effectiveness of the lubricant and its additives in the boundary regime.
Water washout	ASTM D-1264	This test is used to assess the resistance of a grease formulation to displacement from a rolling-element bearing by fresh water under dynamic conditions. Theoretically, one would not expect a particular grease formulation to show deviation beyond the limits inherent in the tests. However, minor changes in grease consistency, within the NLGI grade, could affect results.

equipment. Prescreening can include measurement of special functional properties (electrical or thermal conductivity, index of refraction, viscosity vs. shear rate, etc.), material compatibility measurements (lubricant vs. plastic, elastomer, or solvent), and the effects of low and high temperature extremes on the lubricant.

IX. EXAMPLES OF APPLICATIONS FOR SYNTHETIC GREASES

A. Ball Bearings

Rolling-element bearings represent a major market for synthetic greases. Bearings today are expected to operate over temperatures that may range from 254°C (265°F) to over 200°C (392°F). The application may dictate that the lubricant function during the entire life of the device without the opportunity for relubrication, and precision bearings demand synthetic greases with minimum particulate contamination. For example, ball bearings used for computer spindle applications require greases that provide adequate lubrication under high frequency oscillatory motion, minimize viscous drag, have sufficiently low vapor pressure, are oxidatively stable, are free from particulate matter that may damage the bearing or degrade runout, and do not separate appreciable oil in either dynamic or static mode.

Although all greases exhibit pseudoplastic flow behavior as a function of increasing shear, synthetic sodium-based ester greases become extremely soft during mechanical agitation. Thus this type of grease is ideally suited for bearing applications in which motion of limited amplitude tends to cause lubrication starvation.

Mechanically stable greases do not soften sufficiently to enter the contact zone and thus tend to allow metal-to-metal contact. Viscosity index is a dimensionless parameter used to assess

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a fluid's change in viscosity with temperature. Since most synthetic oils possess a higher viscosity index than nonsynthetics, greases made from high viscosity index oils are able to provide improved film strength over a broader temperature range than petroleum analogues.

Bearings used for computer disk drive applications must also be lubricated with greases that have low vapor pressures. If the lubricant is not sufficiently nonvolatile, lubricant contamination of the storage media could occur, with disastrous results. The vapor pressure of lubricating grease is determined by the molecular weight and molecular weight distribution of its base oil, the specific additives it contains, and its ability to resist degradation by oxygen. Under vacuum conditions, thermo-oxidative stability becomes irrelevant. In the presence of oxygen at elevated temperature, however, lubricants are susceptible to degradation, which during the initial stages liberates low molecular weight fragments that are highly volatile. If thermo-oxidative stability can be ignored, vapor pressure as defined by the Langmuir equation is proportional to surface area, temperature in degrees kelvin, and molecular weight. Vapor pressure in torr can be expressed as follows:

$$P = 17.41\ G\left(\frac{T}{M}\right)^{1/2} \tag{4}$$

where G is the rate of evaporate in grams per centimeter squared per second, T is the temperature in degrees kelvin, and M is the molecular weight of the material. Clearly, under vacuum conditions, the molecular weight of the ingredients in the lubricating grease determines its tendency to volatilize. At 100°C, synthetic hydrocarbon greases made from base oils with a viscosity of 5.8 cSt at 100°C possess vapor pressures that approximate 10^{26} torr. Synthetic greases made from perfluoropolyethers and thickened with polytetrafluoroethylene have vapor pressure below 10^{210} torr at room temperature.

Dirt or contamination in a synthetic lubricating grease is undesirable. Greases employed as lubricants for miniature precision bearings in aerospace systems should contain minimum particulate contaminants, to ensure that lubricating film rupture induced by such contaminants does not cause race or ball damage. The sources of lubricating grease contamination are numerous. However, ultrafiltration is quite effective in removing contaminants greater than 35 μm from most synthetic greases. Some contamination in the 10–34 μm range is usually present in the grease after ultrafiltration and is not usually removed because of concern for the technical merit and cost of doing so. Aside from removing contamination, the ultrafiltration of grease improves homogeneity by increasing dispersion of the grease thickener. Ultrafiltration makes some greases slightly firmer and tends to reduce oil separation. A popular misconception not long ago held that grease filtration through micrometer-sized filters removes the thickener. However, hundreds of grease types have been ultrafiltered in the authors' laboratory without a single incident of gross removal of the thickener. Qualitatively, the actual merits of grease ultrafiltration are somewhat limited; however, evidence is emerging to substantiate the benefits of ultraclean greases in prolonging bearing life and improving performance. A substantial amount of grease intended for high speed spindle applications and aircraft instrumentation is ultrafiltered to cleanliness requirements specified in terms of dirt particle count (ref. 10). Table 11 lists the physical properties of synthetic ester ball-bearing grease used for high speed applications.

For continuous duty at temperatures above 260°C (500°F), for applications requiring a nonflammable grease, or to obtain chemical resistance toward aggressive chemicals like fuming sulfuric acid, only synthetic greases based on perfluoropolyethers and thickened with polytetrafluoroethylene will suffice. Because it is the authors' belief that more oil is better than less for most ball-bearing applications that must see years of trouble-free operation, their view is that fluoroether greases thickened with PTFE oligomers produce superior products. Using the PTFE

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Table 11 Physical Properties of Synthetic Ball-Bearing Grease

Physical property	Typical value
Viscosity of base oil	
At 100°C	8.9 cSt
At 40°C	51 cSt
At −40°C	2550 cSt
Flash point	230°C
Pour point	−55°C
Unworked penetration	260
Worked penetration, 60 strokes	300
Dropping point	202°C
Evaporation, 22 h at 135°C	1.5%
Oil separation, 22 h at 135°C	11.4%
Oxidation stability	
Conditions of test	100 h at 100°C
Pressure drop	<68 kPa
Low temperature torque at −54°C	
Starting	8732 g · cm
After 10 min	2330 g · cm
After 60 min	1150 g · cm
Shell four-ball wear test	
Conditions	1,200 rpm, 40 kg_f load for 1 h
Wear scar at 100°C	0.54 mm
Wear scar at 150°C	0.43 mm
Speedability or DN value	500,000

oligomer, an NLGI grade 2 grease can be prepared with less than 20% thickener, whereas with PTFE micropowder approximately 40% is needed to achieve the same consistency. Any grease containing 40% thickening solids can afford to lose little oil prior to becoming an intractable mass. Table 12 lists typical physical properties of a perfluoropolyether grease.

B. Electrical

One of the most rigorous applications for any synthetic grease is to provide effective lubrication of an electrical switch that produces an electrical arc during on–off cycling. The temperature of an electrical discharge is estimated to be above 1000°C (1832°F), and no present lubricant can cope with such extreme temperatures. However, polyglycol oils thickened with either organic or inorganic thickeners such as amorphous silica are usually the grease of choice for arcing electrical devices, since the polyglycol tends to produce less carbonaceous residue upon thermo-oxidative degradation.

The operation of an electrical switch also places severe demands on grease characteristics. When a switch is closed, the voltage drop within a circuit, if the negligible contact resistance is ignored, is zero. However, as the contact begins to open during switch actuation, the grease must also function as a dielectric if arc damage to the contact is to be minimized. The great dilemma for manufacturers of synthetic grease for electrical switch gear is to design products that tend to remain between the moving contacts during operation without impeding current flow while the switch is energized. To no small degree this simple requirement has remained quite elusive! Lubricants intended for service with electrical contacts must protect the surface

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Table 12 Physical Properties of a Perfluoropolyether Grease

Physical property	Typical value
Color	White
Appearance	Smooth
Unworked penetration	241
Worked penetration, 60 strokes	269
Evaporation, 24 h at 204°C	0.79%
Oil separation, 24 h at 204°C	13%
Four-ball wear test	
Conditions	1200 rpm, 40 kg_f for 1 h
Wear scar at 75°C	0.85 mm
Wear scar at 204°C	1.26 mm
Low temperature torque at −73.3°C	
Starting	2714 g · cm
After 1 h	590 g · cm
Solubility in fuel	None

from oxidation, not from insulating films, and must not be so viscous that electrical continuity cannot be established when the moving elements are at rest.

Electrical connectors represent an entirely different aspect of the successful lubrication of electrical components. Unlike electrical switches, which operate under significant voltage and current, electrical connectors may carry only a few milliamperes of currents driven by millivolts of potential difference. These dry circuits require lubricants that do not impede current flow, that protect the connector interface from environmental corrodants, ease the force required to make or break the connection, and provide years of wear prevention under fretting conditions. Tables 13 and 14 list the properties of two synthetic greases intended for arcing switch and electrical connector applications, respectively.

C. Nuclear

Synthetic greases intended for nuclear service encounter three adversaries: α particles, β particles, and x-rays. All three types of ionizing radiation, if sufficiently abundant, can destroy or-

Table 13 Physical Properties of a Synthetic Grease for Arcing Electrical Switches

Physical property	Typical value
Viscosity of base oil	
At 99°C	30 cSt
At 38°C	526 cSt
Pour point	−34°C
Grease dropping point	225°C
Unworked penetration	334
Worked penetration, 60 strokes	334
Oil separation, 24 h at 100°C	0.8%
Evaporation, 24 h at 100°C	5.0%
Specific gravity at 25°C	0.9
NLGI grade	1

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Table 14 Physical Properties of a Synthetic Grease for Electrical Connectors

Physical property	Typical value
Viscosity of base oil	
At 100°C	40 cSt
At 40°C	400 cSt
Pour point	−34°C
Flash point	316°C
Grease dropping point	260°C
Unworked penetration	310–340
Worked penetration	317

ganic material in a matter of hours or days. Alpha particles, the doubly charged nuclei of helium atoms, are the most aggressive organocides because they are most capable of abstracting hydrogen atoms from the molecules that compose lubricants. Beta particles possessing sufficient kinetic energy can also disrupt the covalent linkages that form the carbon-to-carbon chains in lubricating grease base fluids. On the other hand, x-rays are high energy electromagnetic radiation and are also capable of disrupting the molecular structure of synthetic lubricants. If the flux of the radiation is sufficiently intense, no lubricant would be expected to survive indefinitely; however, silica-based greases prepared from polyphenyl ether are extremely durable toward exposure to ionizing radiation.

Polyphenyl ethers are completely aromatic fluids joined by an ether bridge. The resonance-stabilized aromatic structure of polyphenyl ether oils and a minimum number of vulnerable hydrogen sites are two possible explanations for the unsurpassed resistance to the ravages of ionizing radiation of greases prepared from these fluids.

Grease intended for nuclear service must be virtually free of sulfur, chlorine, and other elements that tend to embrittle steel. Table 15 summarizes the physical properties of a nuclear-capable synthetic grease.

Table 15 Physical Properties of a Synthetic Grease Intended for Nuclear Service

Physical property	Typical value
Viscosity of base oil	
At 99°C	13 cSt
At 38°C	363 cSt
Flash point	288°C
Fire point	349°C
Dropping point of grease	250°C
Unworked penetration	281
Worked penetration, 60 strokes	287
Evaporation, 24 h at 150°C	0.08%
Oil separation, 24 h at 150°C	0.8%

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X. PACKAGING, DISPENSING, AND SOLVENT DISPERSIONS FOR GREASE

A. Packaging and Dispensing Considerations

The consistency of a grease and its oil separation performance can have a significant effect on choice of dispensing equipment in a manufacturing environment. On high throughput manufacturing lines, greases with a consistency of NLGI grade 2 or lower can be handled as quasiliquids and piped under pressure from the point of storage on a manufacturing line to the point of application. Push-plate-style pumps can be used directly on the delivered grease containers to force heavier consistency greases directly into dispensing machinery at the point of use; long piping runs with greases of NLGI grade 3 or greater are not usually feasible because extreme pressure drops are encountered in the lines. In any pressurized delivery system, one must avoid unintended oil separation by removing static pressure from grease lines when flow is stopped over long periods.

In small-quantity precision dispensing applications, several equipment suppliers have developed excellent metering and dispensing technology for grease. The grease can be applied at precise locations, in precisely metered quantities from dollops of fractions of a gram to continuously applied beads of grease. Multiaxis robotic dispensers with custom-designed multihead dispensing needles are available which allow the manufacturing engineer a number of options for incorporating automated grease dispensing into a high speed automated assembly line. Dispensing equipment of this type requires appropriate grease packaging to allow proper interfacing to the automated machinery. Grease customers usually specify cartridge containers in industry standard styles such as Semco® cartridges (from products Research and Chemical Corp.), or syringes from EFD, Inc. Cartridges should be properly filled by the grease manufacturer, using appropriate filtration and deaerating techniques, to avoid particulate contaminants and voids that might cause metering errors or cavitation faults in the dispensing machinery [10].

B. Solvent Dispersions of Greases

Solvent dispersions provide a convenient means for application of a thin coating of grease in a precise manner. This method has been used for many years in the telecommunications industry [11] and is becoming more common in areas such as automotive electronics and precision bearings. The grease is dissolved, partially dissolved, or suspended in an appropriate solvent usually to a concentration by weight of 2–20%. The percent concentration, the solvent evaporation rate, and other factors affect the coating thickness. The choice of solvent is critical in these applications. Until recently, when chlorofluorocarbons (CFCs) were restricted in use because of their ozone depletion potential, CFCs (a.k.a. "Freon," even though the name Freon is a registered trademark of Dupont) were often the grease dispersion solvent of choice. They exhibited excellent solubility with nearly all lubricant base oils, high volatility (important for laying down a uniform grease coating), low toxicity, nonflammability, and reasonably low cost. Other familiar solvents, resorted to upon the departure of Freon from the scene, in most cases represent poor performance in comparison with the banned product. In addition, the bar is continually being raised in the areas of toxicity, ozone friendliness, and a second environmental parameter: global warming potential. A summary of properties required for solvents used in grease dispersions is given in Table 16.

There has been a great deal of product development effort at some of the major chemical companies over the last 10 years in synthesis of new classes of solvents that will satisfy the requirements listed in Table 16. Although the primary focus of these efforts has been finding a replacement for CFCs for industrial cleaning applications, new halogenated solvents are now

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Table 16 Properties of Solvents Used in Grease Dispersions

Property	Desired characteristics
Performance	
Solubilities	Solubility with base oils, additives, and organic gellants desired. If total solubility not achieved, stable (nonagglomerating) dispersion is desired. Best solubility using new halogenated solvents often achieved with solvent blend tailored to dissolve all grease components.
Boiling point/evaporation rate (see Fig. 1)	"Freon-like" is the most common requirement. Low evaporation rates [e.g., isopropanol (IPA), mineral spirits] do not allow uniform coating thickness in many applications. Very high rates (e.g., HCFC-141b) cause excessive depletion of solvent baths, caking of lubricant on applicators, and safety issues with respect to excessive vapor pressures.
Plastic and elastomer compatibility	Some hydrofluorocarbons (HFCs) and HCFCs can attack ester-vulnerable materials. Not usually a concern unless dip-coating an entire assembly is being considered.
Cost	Hydrocarbon solvents and Freon in the $1/lb range. New halogenated solvents in the $10–$50/lb range. Higher costs driving a trend toward solvent vapor recovery.
Safety/environmental	
Flammability	Defined in the United States as having a flash point below 38°C(100°F). Nonflammability is required by customers in a significant portion of grease dispersion applications. This effectively eliminates many hydrocarbon solvents.
Toxicity	Suspected carcinogens (e.g., ketones) are not viable choices for most industrial customers. New halogenated solvents have generally low toxicity.
Ozone depletion potential (ODP)	CFCs no longer available. Most HCFCs are due for phaseout in the 2003–2015 time frame, making them an unpopular choice in new grease dispersion products.
Global warming potential (GWP)	A more recent regulatory parameter. A number of hydrocarbon solvents and some perfluorinated solvents (a subset of fluorinated solvents) are suspect and may face future regulatory restrictions. Most new halogenated solvents are being designed with low GWP in mind.

reaching the marketplace which are suitable for grease dispersions. As yet, there is no new panacea to replace Freon, and grease formulators have instead developed solvent blends that can dissolve certain classes of base oils, gellants, and additives. Even so, except for the absence of a single universal solvent, these solvent blends have all the other requisite properties. For example, in relation to familiar solvents (HCFC-141b, Freon, IP A, and mineral spirits), new halogenated solvents are available with evaporation rates of 0.1–0.2 g/cm^2/h, in the range of Freon, as shown in Fig. 1.

XI. GREASE EDUCATION PROGRAMS

The world of lubricating grease is diverse, and opinions regarding what constitutes a suitable lubricant for a particular application abound. The National Lubricating Grease Institute, head-

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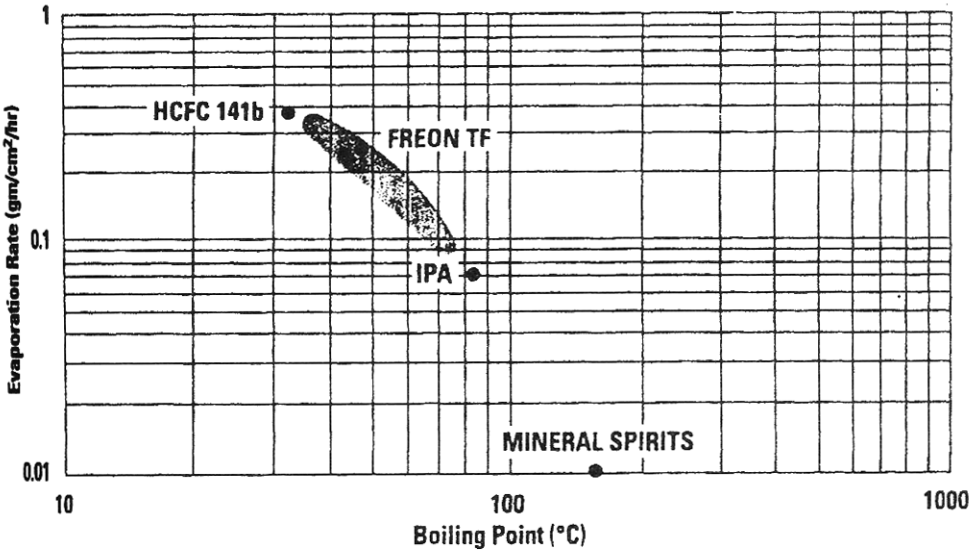

Figure 1 Solvent evaporation rate versus boiling point. (Copyright © 1997, Nye Lubricants, Inc. Used with permission.)

quartered in Kansas City, Missouri, serves as a vehicle bringing manufacturers, users, and distributors together on a yearly basis for information exchanges pertaining to novel products, new performance requirements, and marketing trends. In conjunction with the general program, the institute conducts an education course where some of the country's recognized leaders in grease chemistry and technology serve as instructors. In addition, the institute publishes monthly the *NLGI Spokesman*, the only publication in the country solely dedicated to the understanding of the properties, behavior, and use of lubricating greases. In addition, the Society of Tribologists and Lubrication Engineers (STLE), headquartered in Park Ridge, Illinois, provides similar services across the broader realm of lubricating oil, grease, and tribology. The STLE also puts on an excellent education program in conjunction with the annual society meeting, and publishes articles on lubrication science in its periodical, *Lubrication Engineering*.

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